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Enhancement effects of reducing agents on the degradation of tetrachloroethene in the Fe(II)/Fe(III) catalyzed percarbonate system

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Abstract

In this study, the effects of reducing agents on the degradation of tetrachloroethene (PCE) were investigated in the Fe(II)/Fe(III) catalyzed sodium percarbonate (SPC) system. The addition of reducing agents, including hydroxylamine hydrochloride, sodium sulfite, ascorbic acid and sodium ascorbate, accelerated the Fe(III)/Fe(II) redox cycle, leading to a relatively steady Fe(II) concentration and higher production of free radicals. This, in turn, resulted in enhanced PCE oxidation by SPC, with almost complete PCE removal obtained for appropriate Fe and SPC concentrations. The chemical probe tests, using nitrobenzene and carbon tetrachloride, demonstrated that HO• was the predominant radical in the system and that O₂^{•-} played a minor role, which was further confirmed by the results of electron spin resonance measurements. PCE degradation decreased significantly with the addition of isopropanol, a HO• scavenger, supporting the hypothesis that HO• was primarily responsible for PCE degradation. It is noteworthy that Cl⁻ release was slightly delayed in the first 20 mins, indicating that intermediate products were produced. However, these intermediates were further degraded, resulting in the complete conversion of PCE to CO₂. In conclusion, the use of reducing agents to enhance Fe(II)/Fe(III) catalyzed SPC oxidation appears to be a promising approach for the rapid degradation of organic contaminants in groundwater.

Keywords

Tetrachloroethene (PCE); Sodium Percarbonate (SPC); reducing agents; Hydroxyl radical (HO•)

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1. Introduction

Chlorinated solvents are carcinogenic and often biorefractory in natural environments. **Tetrachloroethene** (PCE), one typical chlorinated solvent frequently found in contaminated groundwater, has been listed as a priority pollutant by the United States Environmental Protection Agency (EPA) [1] and possesses acute and chronic toxicity to humans and animals. The maximum contaminant level of PCE in groundwater has been set at $5 \mu\text{g L}^{-1}$ [2]. To date, numerous methods have been investigated for remediation of soil or groundwater contaminated by chlorinated solvent compounds. In situ chemical oxidation (ISCO) technologies, employing oxidants such as permanganate [3–6], ozone (O_3) [7], Fenton reagents ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) [8, 9], and sodium persulfate [10–12], have become a popular method. Of these, the Fenton process and some modified Fenton systems have one of the highest reactivities and potential for the destruction of a large range of contaminants.

In the traditional Fenton reaction, the well recognized mechanism is the decomposition of H_2O_2 to hydroxyl radicals ($\text{HO}^\bullet$) induced by Fe(II) (Eq. 1, rate constant obtained at 20–25 °C and 1 atm) [13].

$\text{HO}^\bullet$ is a powerful oxidant with a redox potential of 2.76 V [11]. Therefore, it reacts with most organic compounds rapidly, with second order rate constants ranging from 10^7 to $10^{10} \text{M}^{-1} \text{s}^{-1}$ [14]. However, there are significant drawbacks with the conventional Fenton system. The first one is the requirement for acidic pH conditions ($\text{pH} = 2\text{--}4$ [15]), which is undesirable and generally impractical for field applications because the pH of natural groundwater is often near neutral or slightly alkaline. Another major limitation is the accumulation and precipitation of Fe(III) , which can reduce reaction rates. One of the common modified Fenton reactions involves the use of Fe(III) to catalyze H_2O_2 . In the homogeneous $\text{Fe(III)}/\text{H}_2\text{O}_2$ system, the spontaneous reaction between H_2O_2 and Fe(III) primarily forms Fe(III) -hydroperoxy complexes (Eq. 2). The Fe(III) -hydroperoxy complexes are further decomposed to Fe(II) (Eq. 3) [16–18] and then perhydroxyl radicals ($\text{HO}_2^\bullet$) and superoxide anion radicals ($\text{O}_2^{\bullet-}$) are produced (Eq. 4).

According to Eqs. (2) and (3), the production of Fe(II) is well controlled in the $\text{Fe(III)}/\text{H}_2\text{O}_2$ system, which leads to the slow decomposition of H_2O_2 and generation of $\text{HO}^\bullet$. However, the low solubility of Fe(III) at neutral pH and rapid oxidation of Fe(II) in the $\text{Fe(III)}/\text{H}_2\text{O}_2$ system requires reducing agents to enhance the presence of Fe(II) in solution.

In our previous work [19], sodium percarbonate (SPC, $\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$) has been applied as a replacement for H_2O_2 in the chemical oxidation of PCE. SPC possesses similar function as liquid H_2O_2 , such that free H_2O_2 is released into solution when percarbonate is mixed with water (Eq. 5).

SPC has many advantages for use as an oxidant [20, 21]: 1) it is suitable for a wide pH range; 2) it is safer to handle and transport; 3) it does not introduce any chemicals into the water matrix that would be considered toxic besides H_2O_2 ; and 4) percarbonate acts as a base, raising the pH when introduced into water and even leading to a buffering effect that can prevent the undesired reduction in pH. However, it has shown limited effectiveness in some cases [22].

The objectives of this study are to explore the role of reducing agents in the redox cycle of Fe(III)/Fe(II) for the Fe catalyzed SPC system, and to elucidate the degradation mechanism of the modified Fe catalyzed SPC system. The following reducing agents, hydroxylamine hydrochloride (HAH), sodium sulfite (SS), l-ascorbic acid (ASC), and sodium ascorbate (SA) were tested for the purpose of reducing Fe(III) to Fe(II). As a common reducing agent for Fe (III), hydroxylamine is used in total iron determination [23]. In recent years, several studies have introduced hydroxylamine hydrochloride into the Fenton-like oxidation for the remediation of waste water and significant enhancement was observed [24, 25]. Sodium sulfite is widely used in water treatment as an oxygen scavenger agent. Ascorbic acid is naturally present in most fruits and vegetables. It is also a natural antioxidant and widely employed in the agricultural, pharmaceutical, and food industries. ASC is a dibasic acid, and may serve as a two-electron reductant with a redox potential of -0.06 V [26]. To the best of our knowledge, the use of reducing agents to modify the Fe catalyzed SPC system has not yet been reported. It is hypothesized that the addition of reducing agents to the Fe catalyzed SPC system will accelerate the redox cycle of Fe (III) to Fe (II), and thereby reduce Fe(III) accumulation. To investigate the mechanism of PCE degradation in these systems, the dominant free radicals were detected by using free radical probe compounds and free radical scavengers. Electron paramagnetic resonance (EPR) was used to further identify the radicals involved in PCE degradation. Lastly, the complete conversion of PCE to CO_2 during its degradation was assessed through the measurement of the Cl^- release rate using ion chromatography.

2. Materials and methods

2.1. Materials

The following reagents were purchased from Aladdin (Shanghai, China) and used without further modification: tetrachloroethene (PCE, C_2Cl_4 , >99.0%), carbon tetrachloride (CT, CCl_4 , >99.5%), isopropanol ($(\text{CH}_3)_2\text{CHOH}$, >99.5%), nitrobenzene ($\text{C}_6\text{H}_5\text{NO}_2$, >99.0%), chloroform (CHCl_3 , >99.0%), iron (II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, >99.0%), ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$, >99.0%), hexane (C_6H_{14} , >97%), hydroxylamine hydrochloride (HAH, $\text{NH}_2\text{OH} \cdot \text{HCl}$, >99.0%), sodium sulfite (SS, Na_2SO_3 , >99.0%), l-ascorbic acid (ASC,

$C_6H_8O_6$, >99.0%), sodium ascorbate (SA, $C_6H_7NaO_6$, >99.0%). Sodium percarbonate (SPC, $Na_2CO_3 \cdot 1.5H_2O_2$, >98%) was purchased from Acros Organics (Shanghai, China). 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) was purchased from Sigma (Shanghai, China). Ultrapure water from a Milli-Q water process (Classic DI, ELGA, Marlow, U.K.) was used for the preparation of aqueous solutions.

2.2. Experimental procedures

PCE stock solution was prepared by equilibrating neat PCE with ultrapure water overnight under gentle stirring in the dark. The PCE stock solution was then diluted to 0.12 mM (approximately 20 mg/L). Batch tests were conducted using a 250 mL cylindrical glass reactor. PCE in deionized water was used for these experiments to facilitate implementation and monitoring of the reducing-agent-induced cycling of Fe. Studies with actual groundwater will be performed in the future. The pre-set dosages of $Fe_2(SO_4)_3$ and reducing agents were added to the PCE solution and thoroughly mixed immediately using a magnetic stirrer, then the pre-set dosage of SPC was added to start the reaction. The concentrations for all reagents used are reported in the figure captions. The pH of the solution was unadjusted, and the temperature was constant at 20 °C. Aqueous samples were collected at the desired time intervals and analyzed immediately, and the tests were conducted in triplicate and the mean values were reported.

EPR detection was conducted to confirm the main free radicals present in the catalyzed SPC system. The compound 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) was used to trap the free radicals in solution. Samples (1.0 mL) were collected at the desired time and thoroughly mixed with 1.0 mL DMPO solution (8.84 mM) for 1 min. The solution was then transferred to a capillary tube with a microinjector for analysis with the EPR instrument. The high performance liquid chromatography (HPLC) technique was used to measure the hydroxylated products of salicylic acid. 2,3-dihydroxybenzoic acid (DHBA) and 2,5-DHBA can be directly measured by the HPLC system (Ultimate 3000, Dionex, USA) coupled with amperometric detection. Intermediate products were detected using gas chromatography mass spectrometry (GC/MS).

2.3. Analytical methods

Aqueous samples (1.0 mL) were withdrawn at predetermined time intervals and then extracted with hexane (1.0 mL) for 3 min using a vortex stirrer. After standing for 5 min, the organic phase (PCE in hexane) was transferred to a 2-mL GC vial. The concentrations of PCE and CT in hexane were analyzed using a gas chromatograph (Agilent 7890A, Palo Alto, CA) equipped with an electron capture detector (ECD), an auto-sampler (Agilent 7693), and a DB-VRX column (60-m length, 250- μ m i.d., 1.4- μ m thickness). The temperatures of the injector and detector were 240 °C and 260 °C, respectively, and the oven temperature was kept constant at 120 °C. The amount of sample injected was 1.0 μ L with a split ratio of 40:1. The recovery of PCE through the above procedure was in the range of 87–95%. The concentration of NB was analyzed using a gas chromatograph (Agilent 7890A, Palo Alto, CA) equipped with a flame ionization detector (FID), an auto-sampler (Agilent 7693), and an HP-5 column (30-m length, 320- μ m i.d., 0.25- μ m thickness). The temperatures of the injector and detector were 200 and 250 °C, respectively, and the oven

temperature was constant at 170 °C. The amount of sample injected was 1.0 µL with a split ratio of 1:1. The chloride anion was analyzed by ion chromatography (Dionex ICS-I000, Sunnyvale, CA). The free radicals were identified by EPR (EMX-8/2.7C, Bruker, Germany) using DMPO as a spin trap. All spectra were obtained under the following conditions: field sweep, 100 G; microwave frequency, 9.866 GHz; microwave power, 2.016 mW; modulation amplitude, 1 G; conversion time, 40.96 ms; time constant, 163.84 ms; and receiver gain, 3.17×10^4 . GC/MS employed an Agilent technologies 7890A GC with Quattro micro MS column: DB-5 (30 m, 0.25 mm, 0.25 mm) column. The amount of sample injected was 1.0 µL with a split ratio of 10:1. The oven temperature programming was: 30 °C for 4 min and then 30 °C min⁻¹ to 75 °C then 45 °C min⁻¹ to 275 °C. The pH was measured using a pH meter (Mettler-Toledo, DELTA 320, Greifensee, Switzerland).

The concentrations of soluble ferrous ion (Fe(II)) were determined according to the 1,10-phenanthroline method [27]. Hydrogen peroxide (H₂O₂) was determined using the TiCl₄ spectrophotometric method [28]. No interferences were observed with the concentrations of ferric ions used.

3. Results and discussion

3.1 The effect of reducing agents on PCE degradation in Fe(III)/SPC and Fe(II)/SPC systems

According to our previous research, both Fe(III) (Fig. S1 in Appendix A. Supplementary data) [29] and Fe(II) catalyzed SPC systems [19] can degrade PCE effectively. However, the degradation rate is significantly different because of different PCE degradation pathways as well as the different concentrations of Fe(II) present. Therefore, we introduced reducing agents into these two systems for the purpose of comparing their impact on PCE degradation. Fig. 1 presents the results of PCE degradation in Fe(III)/SPC and Fe(II)/SPC systems in the presence of different reducing agents.

Significant decreases in PCE concentrations were observed for most of the reducing agents for the Fe(III)-catalyzed SPC system (Fig. 1a). In contrast, only ~12% PCE degradation was observed for the control test, which contained 0.5 mM Fe(III) and 0.5 mM SPC (control curve in Fig. 1). The addition of reducing agents to the Fe(III)/SPC system clearly enhanced the rate of PCE degradation. For example, the magnitude of PCE degradation in 5 min increased from approximately 4% to 98%, 53%, 59% and 10% for the HAH, SS, ASC and SA reagents, respectively. The much slower rate of degradation observed for the control is consistent with the results of previous research [29], which demonstrated that more than 30 min was required for the complete degradation of PCE in the Fe(III)/SPC system in the absence of reducing agents, even when high concentrations (10 mM) of Fe(III) and SPC were used.

As explained in the introduction section, the Fe(III) species can be reduced to Fe(II) by H₂O₂ and HO₂[•], as shown in Eqs. 2–3 and Eq. 6 [25]:

In the Fenton-like process, the Fe(III)/Fe(II) redox cycle rate is much slower than that of the production of HO• via the reaction in Eq. (1), which limits the rate of contaminant degradation. In contrast, in the present reducing-agent-modified Fe(III)/SPC systems, PCE degradation showed a rapid-reaction period in the initial 5 minutes and then slowed down sharply to a nearly static period. This behavior is hypothesized to result from the relatively higher initial concentration of Fe(II) and the accelerated recycling of Fe(II) in the presence of the reducing agents (Fig. 2). In the static period, the concentration of Fe(II) is relatively low, leading to the limited production of HO•. Theoretically, HO• was scavenged by the reducing agents. Therefore, we speculate that the accelerating effect might play a more dominant role than the scavenging effect during the rapid-reaction period. In contrast, the scavenging effect terminated the reaction in the static period. In summary, HAH, ASC and SS were particularly effective in terms of PCE degradation enhancement for the Fe(III)/SPC system.

PCE degradation was also significantly enhanced when HAH was introduced into the Fe(II)/SPC system (Fig 1b). Conversely, SS, ASC and SA actually reduced the rate and magnitude of PCE degradation (Fig 1b). This is because, on the one hand, the introduction of reducing agents enhanced the production of HO• which is the primary free radical contributing to the degradation of PCE. On another hand, as discussed above, the capability for HO• scavenging by SS, ASC, and SA is higher than that by HAH [25]. Thus, the quenching effect produced by SS, ASC, and SA was stronger than their impact on accelerating the recycling of Fe(II) in the Fe(II)/SPC system, which overall led to decreased PCE degradation.

The concentration of Fe(II) and H₂O₂ were measured in the modified systems to help elucidate the effect of the reducing agents on the PCE degradation process. Fig.2 indicates that the concentration of Fe(II) was much higher when HAH and ASC were added to the Fe(III)/SPC system in comparison to the control. Correspondingly, the concentration of H₂O₂ was lower. Similar phenomenon was also observed for the HAH modified Fe(II)/SPC system. However, in the SS modified Fe(III)/SPC system, the concentration of Fe(II) was slightly higher than that in the control during the first 1 min, and later was similar. In contrast, the concentration of H₂O₂ was much higher than for the other treatments with 60% of H₂O₂ remaining after 60 min reaction (see inserted Figure in Fig. 3). These results indicate that HAH and ACS could significantly enhance the recycling of Fe(II) and maintain relatively high levels of Fe(II) for a long time.

As mentioned above, other than the acceleration of Fe(III)/Fe(II) recycling to enhance PCE degradation, reducing agents were capable of quenching the radicals with high reaction rate, for example, HAH and ASC can serve as HO• scavengers with reaction rates of $9.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ [30] and $1.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ [25], respectively. Furthermore, the inorganic anions generated in the system may also contribute to HO• scavenging [31–33]. To investigate the effect of reducing agent concentration on PCE degradation, batch experiments were conducted in the presence of 1.0, 2.0, and 5.0 mM of reducing agents and 0.5 mM of Fe(III) and SPC each (Fig. S2). The results showed that the degradation of PCE was inhibited when excessive reducing agents were added. For example, when the concentration of Fe(III) and SPC were fixed at 0.5 mM, the final PCE degradation decreased from 59% to 5% as the

ASC concentration increased from 1 mM to 5 mM. Similar results were obtained for the HAH modified Fe(II)/SPC system (Fig. S3). These results can be attributed to the HO[•] quenching effect of excessive reducing agents and anions. Therefore, an appropriate dosage of reducing agent is required when it is applied in practice. In our case, the highest degradation rates were obtained when 1 mM of reducing agent was added, equivalent to an optimal molar ratio of Fe to reducing agent of 1:1.

The concentrations of catalyst and oxidant were demonstrated to be crucial for the conventional Fenton system [34–36]. For the purpose of investigating the influence of Fe and SPC concentration on PCE degradation, additional batch experiments were conducted in the presence of 0.5, 1.0 and 5.0 mM of Fe(III) and SPC for the Fe(III)/SPC system (Fig. S4). In the HAH modified Fe(III)/SPC system, 0.5 mM of Fe(III) and SPC were shown to be sufficient for the complete removal of PCE and no negative effect was observed when excessive Fe(III) and SPC were applied. In the presence of ASC and SA (Fig. S4c, S4d), the degradation rate of PCE increased as Fe(III) and SPC concentrations were increased, ultimately resulting in complete removal. These results suggest that, in terms of the complete degradation of PCE, the addition of HAH, SS, ASC, and SA are all effective.

3.2 Identification of free radicals using free radical probe tests

Although HO[•] has been recognized as the most active species in the conventional Fenton reaction, the generation of other reactive oxygen species, such as O₂^{•-}, HO₂[•] and hydroperoxide anion (HO₂⁻), have also been observed in some modified Fenton systems [37, 38]. Theoretically, O₂^{•-} is a weak reductant that reacts with CT at a rate constant of 3800 M⁻¹ s⁻¹ in dimethyl sulfoxide [39]. Teel et al. [39] and Smith et al. [40] demonstrated that O₂^{•-} is the primary reductive species in modified Fenton's reagent responsible for CT destruction. Therefore, it is quite possible that under specific conditions, both oxidation and reduction reactions may simultaneously contribute to the degradation of contaminants in the modified Fe(II)/SPC and Fe(III)/SPC systems. Hence, further investigations were conducted in this study to identify the yields of HO[•] and O₂^{•-} using the chemical probe method.

Several chemicals were selected as probe compounds according to their reactivity with each of the reactive oxygen species potentially present in the modified Fe(III)/SPC system. Nitrobenzene (NB) and CT were selected as the HO[•] and O₂^{•-} probe compounds, respectively, because NB possesses high reactivity with HO[•] (k_{HO•} = 3.9 × 10⁹ M⁻¹ s⁻¹) [41] and CT reacts with reductants rapidly (k_{HO•} < 2 × 10⁶ M⁻¹ s⁻¹, k_e = 1.6 × 10¹⁰ M⁻¹ s⁻¹) [42]. The initial concentrations of NB and CT were 2 mM and 0.05 mM, respectively, and the initial concentrations of SPC and Fe were both 5.0 mM. The generation of HO[•] in the Fe(III)/SPC systems with 5.0 mM of HAH, SS, and ASC added, quantified through NB degradation, is shown in Fig. 4. The results indicate that HO[•] was present in these systems, which led to a rapid degradation of NB. The degradation of NB was also significant in the HAH modified Fe(II)/SPC system. This is consistent with the significant PCE degradation observed for the HAH modified Fe(II)/SPC system, further confirming that the level of HO[•] was much higher than that in the other systems. The degradation of NB in HAH and ASC modified Fe(III)/SPC systems were a little higher than that in the SS modified Fe(III)/SPC system. These results are consistent with the results discussed above (Fig. 1–3).

The generation of reductants in SPC systems with 1.0 mM of HAH, SS and ASC added, quantified by CT degradation, is shown in Fig. 4b. Similar magnitudes of CT degradation (approximately 15%–20% degraded in 60 min) were observed for the modified systems, all of which are larger than the minimal degradation observed for the control. These results suggest that $O_2^{\bullet-}$ were present at similar levels in all of the modified systems and played a minor role in the degradation of NB.

Based on the results discussed above, it is deduced that both the oxidant $HO^\bullet$ and the reductant $O_2^{\bullet-}$ were present in the HAH modified Fe(II)/SPC and the HAH, SS, ASC modified Fe(III)/SPC systems. These observations are in agreement with the results discussed in sections 3.3 and 3.4.

3.3 Elucidation of the role of free radicals using free radical scavengers

As reported, PCE can be degraded by both $HO^\bullet$ and $O_2^{\bullet-}$ radicals [43, 44], but its degradation by $HO^\bullet$ ($k_{HO^\bullet} = 3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) is significantly faster than by $O_2^{\bullet-}$ ($k = 15.0 \pm 4.5 \text{ M}^{-1} \text{ s}^{-1}$ in dimethyl formamide). To elucidate the role of $HO^\bullet$ and $O_2^{\bullet-}$ in the HAH, SS and ASC modified Fe(III)/SPC systems and the HAH modified Fe(II)/SPC system, experiments were conducted independently with the addition of different free radical scavengers. Isopropanol was used to scavenge $HO^\bullet$ because it reacts rapidly with oxidants ($k_{HO^\bullet} = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and significantly more slowly with reductants ($k_e = 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$). Chloroform was used as a scavenger of $O_2^{\bullet-}$, because chloroform possesses relatively weak reactivity with $HO^\bullet$ ($k_{HO^\bullet} = 7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) and high reactivity with reductants ($k_e = 3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) [39]. Isopropanol and chloroform were added to the solution in 2 mM, which is approximately 16 fold higher than the molar concentration of PCE. Control treatments were also conducted in parallel without a scavenger. The results are shown in Fig. 5.

The magnitudes of PCE degradation in 5 min were 98%, 53%, 59% and 95% in the HAH, SS, and ASC modified Fe(III)/SPC systems and HAH modified Fe(II)/SPC system, respectively, in the absence of isopropanol. In contrast, PCE degradation was significantly inhibited in the presence of isopropanol, with 5-min degradation magnitudes reduced to 7%, 5%, 1% and 9% correspondingly. These results indicate that $HO^\bullet$ was dominant in these systems, but other non- $HO^\bullet$ mechanisms that cause PCE degradation may simultaneously occur.

PCE degradation in the HAH, SS, and ASC modified Fe(III)/SPC systems and HAH modified Fe(II)/SPC system scavenged by excess chloroform are also shown in Fig. 5. PCE degradation was reduced to different degrees by adding 2 mM of chloroform. For example, PCE degradation in 5 min was reduced to approximately 80%, 48%, 47% and 2% in the HAH, SS, and ASC modified Fe(III)/SPC systems and HAH modified Fe(II)/SPC system, respectively. These results indicate that $O_2^{\bullet-}$ participated in the degradation of PCE.

The results presented above suggest that PCE was primarily degraded by $HO^\bullet$ in the HAH, SS and ASC modified Fe(III)/SPC systems and HAH modified Fe(II)/SPC system, and that $O_2^{\bullet-}$ played a minor role in PCE degradation.

3.4 Detection of free radicals

For the purpose of confirming the primary radicals that contributed to the degradation of PCE, electron paramagnetic resonance (EPR) was used to detect HO• by measuring the intensity of the DMPO-OH adducts signal (Fig. 6). The specific spectrum (quartet lines with peak height ratio of 1:2:2:1) was obtained with high intensity in the Fe(II)/SPC, HAH modified Fe(II)/SPC, HAH, SS and ASC modified Fe(III)/SPC systems (Fig. 6). The addition of reducing agents significantly enhanced the production of HO• in Fe(III) catalyzed SPC systems. The intensity of HO• in HAH modified Fe(II)/SPC system was about 2 fold greater than that in the HAH and ASC modified Fe(III)/SPC systems. The EPR spectra are consistent with those reported for HO• in our previous study [19]. These results, together with the result discussed above, showed that HO• was the predominant oxidant in the HAH modified Fe(II)/SPC, HAH, SS and ASC modified Fe(III)/SPC systems. However, O₂^{•-} was not detected during the EPR analyses, which could be attributed to the relatively minor concentrations of O₂^{•-} in these systems.

Based on the EPR results, the concentration of HO• was further measured using the salicylic acid hydroxylation method [45] for the purpose of determining the HO• production pattern. HO• can attack salicylic acid and produce 2,3-DHBA and 2,5-DHBA that can be measured directly by HPLC (see Fig.S5S). Therefore, salicylic acid was used to measure the concentration of HO• because of its high reaction rate ($2.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) [45] and the stability of 2,3-DHBA and 2,5-DHBA. Fig. 7 and Fig. 8 show the chromatograms of samples of salicylic acid solution after reaction (60 min) and the total concentration of HO• at different reaction time in Fe(III)/HAH, Fe(III)/ASC and Fe(II)/HAH systems. The results indicate the quick production of HO• in the first 5 min, which is consistent with the observed PCE degradation. Among the systems, the HO• concentration in Fe(II)/HAH system was highest, which is also consistent with the EPR results. However, the HO• concentration (about 0.09–0.15 mM) is much less than the initial SPC concentration (0.5 mM), which theoretically contains 0.75 mM of H₂O₂. This may because of the presence of HO• scavenging reaction (Eq. 7–9).

3.5 The complete conversion of PCE

The Cl⁻ concentration in aqueous solution is an effective indicator for PCE destruction. Therefore, it was analyzed and the chlorine mass balance was calculated to confirm the dechlorination extent of PCE in the HAH modified Fe(II)/SPC, HAH, SS and ASC modified Fe(III)/SPC systems to confirm whether intermediate products are formed. Theoretically, 1 mol of PCE produces 4 mol of Cl⁻ after complete dechlorination. The concentration of Cl⁻ for HAH addition was detected before addition of SPC, and this was treated as the

background value. Fig. 9 shows that the dechlorination of PCE occurred simultaneously with the degradation of PCE. However, Cl^- release was slightly delayed, which may indicate the presence of intermediate products. The final measured Cl^- release rate was highly consistent with the theoretical Cl^- release rate for complete conversion after a 20-min reaction period. This suggests that the possible intermediate products were further degraded within 20 min. These results are similar to those reported in our previous study [19], in which Fe(II) was used as the catalyst. Unfortunately, further GC/MS detection did not detect any chlorinated organic compound except PCE (Fig.S6). The above results indicate that PCE can be degraded completely to CO_2 in the HAH modified Fe(II)/SPC, HAH, SS and ASC modified Fe(III)/SPC systems. The primary reaction occurred in the degradation process may be the oxidation of PCE by $\text{HO}^\bullet$ as shown in Eq. (10).

4 Conclusion

In this study, the impact of adding reducing agents to enhance Fe(II) or Fe(III) catalyzed SPC degradation of PCE was investigated. It is hypothesized that the addition of common reducing reagents hydroxylamine hydrochloride, sodium sulfite, ascorbic acid and sodium ascorbate accelerated the recycling of Fe(II) from Fe(III), thereby enhancing PCE degradation. However, insufficient reducing agent dosage would result in poor oxidation ability, but excessive reducing agent also would lead to the decline of oxidation efficiency because of the capability for $\text{HO}^\bullet$ scavenging by reducing agents and the anions introduced by them. Almost complete PCE removal was obtained when appropriate Fe and SPC were applied in the systems.

To identify the active radical species, two probe compounds, nitrobenzene (NB) and carbon tetrachloride (CT), were added to the system. Differences between the reactivity of the probes and the potential radical species were observed, suggesting that $\text{HO}^\bullet$ was the predominant radical and that $\text{O}_2^{\bullet-}$ provided a minor contribution. The EPR data further indicated that $\text{HO}^\bullet$ was the predominant radical responsible for PCE oxidation. Nearly complete release of chloride suggested that PCE was completely converted to CO_2 . In conclusion, the results show that the addition of reducing agents to enhance Fe catalyzed by SPC is an effective method for improving the treatment of organic contaminant in water.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig.1.

Impact of reducing agents on PCE degradation by Fe(III) or Fe(II) catalyzed sodium percarbonate: PCE = 0.12 mM, SPC = 0.5 mM, reducing agent = 1 mM, a) Fe(III) = 0.5 mM; b) Fe(II) = 0.5 mM

Fig.2.

Concentration of soluble Fe(II) in different systems: SPC = 0.5 mM, reducing agent = 1 mM, Fe(III) = 0.5 mM, Fe(II) = 0.5 mM

Fig.3. Concentration of H_2O_2 in different systems: SPC = 0.5 mM, reducing agent = 1 mM, Fe(III) = 0.5 mM, Fe(II) = 0.5 mM; Inserted figure: the H_2O_2 molar percentage after 60 min of reaction

Fig.4.

Impact of reducing agents on NB and CT degradation performance in different systems:
 SPC = 5 mM, Fe = 5 mM, reducing agents = 5 mM; a) NB = 2 mM; b) CT = 0.5 mM

Fig.5.
Effect of isopropanol and chloroform on PCE degradation performance: PCE = 0.12 mM,
Fe(III) = 0.5 mM, SPC = 0.5 mM, Isopropanol = 50 mM, Chloroform = 2 mM

Fig.6.
EPR spectrum of different systems at 1 min reaction time

Fig.7. Salicylic acid hydroxylation as an indicator of hydroxyl radical generation: Chromatograms of an authentic standard containing 2,3-DHBA, 2,5-DHBA and salicylic acid (0.33 mM each) (a) and chromatograms of samples of salicylic acid solution after reaction (60 min) in Fe(III)/HAH (b), Fe(III)/ASC (c), and Fe(II)/HAH (d) systems (Fe(III) and Fe(II) = 0.5 mM, SPC = 0.5 mM, HAH and ASC = 0.5 mM)

Fig.8. Total hydroxyl radical production in Fe(III)/HAH, Fe(III)/ASC, and Fe(II)/HAH systems (Fe(III) and Fe(II) = 0.5 mM, SPC = 0.5 mM, HAH and ASC = 0.5 mM)

Fig.9.
PCE degradation and release of Cl^- versus treatment time